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(54) ORGANIC THIN FILM ELECTROLUMINESCENT ELEMENT

(57)Abstract:

PURPOSE: To provide the subject element excellent in luminescent efficiency and durability and useful for display elements, etc., by nipping a specific organic thin layer luminescent layer between a pair of electrodes one of which is transparent.

CONSTITUTION: The objective element is characterized by nipping an organic thin film luminescent layer between a pair of electrodes one of which is transparent, the luminescent layer comprising the lamination product of two or more layers of the same polymeric luminescent substance having a polyparaphenylene vinylene skeleton or polynaphthovinylene skeleton, one or more of the luminescent substance layers being a charge-injected layer doped with a polymeric dopant.

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(54)【発明の名称】 有機薄膜エレクトロルミネッセント素子

(57)【要約】

【構成】 少なくとも一方が透明である一対の電極間に、有機薄膜発光層を挟持してなる有機薄膜型エレクトロルミネッセント素子において、前記発光層が同一の高分子発光体を少なくとも2層積層したものであって、前記発光体層の少なくとも一つは高分子ドーパントがドーブされた電荷注入層であることを特徴とする有機薄膜エレクトロルミネッセント素子。

【効果】 有機EL素子に長寿命を賦与するきわめて簡便な手法で、塗布成膜法という製造工程で製造でき、発光効率が高く、耐久性を兼備した有機薄膜エレクトロルミネッセント素子である。

(2)

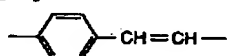
1

## 【特許請求の範囲】

【請求項 1】 少なくとも一方が透明である一対の電極間に、有機薄膜発光層を挟持してなる有機薄膜型エレクトロルミネッセント素子において、前記発光層が同一の高分子発光体を少なくとも 2 層積層したものであって、前記発光体層の少なくとも一つは高分子ドーパントがドーブされた電荷注入層であることを特徴とする有機薄膜エレクトロルミネッセント素子。

【請求項 2】 発光体が構造式 [1]

【化 1】

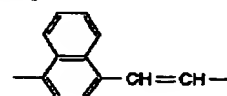


[1]

で表されるポリパラフェニレンビニレン骨格を有する高分子化合物である請求項第 1 項に記載の有機エレクトロルミネッセント素子。

【請求項 3】 発光体が構造式 [2]

【化 2】



[2]

で表されるポリナフトビニレン骨格を有する高分子化合物である請求項第 2 項に記載の有機エレクトロルミネッセント素子。

【請求項 4】 発光層が塗布法により形成されてなる層である請求項第 3 項または第 4 項に記載の有機エレクトロルミネッセント素子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は有機薄膜エレクトロルミネッセント（以下 EL と略す。）素子に関する。更に詳しくいえば、高輝度、高効率の発光特性を有し、面状の光源や表示素子として利用可能な有機薄膜 EL 素子に関する。

【0002】

【従来の技術】 EL 素子は電界発光素子とも呼ばれ、面状発光体としての応用研究が広汎に行なわれている。この EL 素子は発光励起機構の違いによって 2 つに大別される。1 つは、強い電界の印加のみで発光する、いわゆるデストリオ (Destriau) 効果に基づく真性 (固有) EL 素子であり、他の 1 つは、点接触ダイオード、または p n 接合に順電流を流すことにより発光する、いわゆるロゼフ (Lossev) 効果に基づく電荷注入型 EL である。

【0003】 前者は Zn S、Cd S 等の II-VI 族化合物半導体に、Mn、Cu、希土類元素等の発光中心 (活性素) となる元素を添加分散した系が一般的であり、ホットエレクトロンによる活性素励起が基本的発光機構と考えられている。この種の EL 素子に関する研究は長い歴史と実績を持っており、分散型素子は既に実用化されており、1970 年代以降、薄膜型素子の研究も盛んに行なわ

2

れてきた。

【0004】 しかしながら、上記の無機材料からなる EL 素子は、駆動に 200 V もの高電界印加が必要なこと、周辺駆動回路の製造コストが高く、耐久性、輝度が不十分なこと、多色化が困難なこと等多数の問題点を抱えている。

【0005】 一方、電荷注入型 EL 素子については、縮合多環芳香族炭化水素を中心とした有機化合物を対象に古くから研究が行なわれているが、1970 年代終りになって実用的見地からの取り組みがなされてきた。電荷注入型 EL 素子の最大の特徴は、前記真性 EL 素子に比べて低い電圧での駆動が可能な点にある。

【0006】 1980 年代後半に至って、真空蒸着成膜による材料の均一薄膜化と電荷注入層、発光層の積層多層化により、有機薄膜を発光体とする電荷注入型 EL 素子が、高輝度、高効率な優れた面状発光素子となり得ることが実証された (例えば、C. W. Tang et al., Appl. Phys. Lett., 51, 913 (1987), C. Adachi et al., Jpn. J. Appl. Phys., 27, L269 (1988)、特開昭 59-194393、米国特許 4,720,432 等)。また、有機材料特有の分子設計の多様性を活かして、置換基導入による多彩な色調制御が可能であり、無機材料の真性 EL 素子では望むべくもない EL 発色の色揃えができることも示されている (C. Adachi et al., Appl. Phys. Lett., 56, 799 (1990))。

【0007】 これら有機薄膜型 EL 素子は、一部素子特性では実用レベルを凌駕する程の瞎目すべき性能が得られるものの、寿命が短く、耐久性が乏しいという大きな欠点を持っている。これは真空蒸着膜では、経時的にあるいは通電によって分子の凝集が起って不均一化する事に主たる原因があり、均一蒸着成膜能の要求が材料選択に厳しい制限を加えることと相俟って、実用化への障害を深刻なものにしている。

【0008】 有機 EL 素子の特長を活かしつつその長寿命化を達成する為の有力な手段として、材料を高分子体化することが考えられる。最近、ポリパラフェニレンビニレン (PPV) での EL 発光が確認され (J. H. Burroughes et al, Nature, 347, 539 (1990), WO-9013148 等)、また電荷注入層に導電高分子を応用する試みも行なわれている (S. Adachi et al., Jpn. J. Appl. Phys., 25, L773 (1986))。他方、発光層と電荷注入層を一体化した混合薄膜を用いる等の手段も講じられている (文献があれば加入してください。)。しかしながら、いずれも十分な素子特性および寿命を得るに至っておらず、実用域には程遠いのが現状である。

【0009】

【発明が解決しようとする課題】 従って、本発明は上記問題点を解決し、高輝度、高効率な特性と充分な耐久性を兼備する有機薄膜型 EL 素子を提供することを目的とするものである。

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## 【0010】

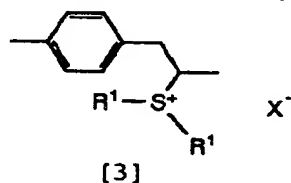
【課題を解決するための手段】本発明者らは、有機薄膜型エレクトロルミネッセント素子において、所要の耐久性を実現する為には素子構成材料の高分子体化が必須要件であるとの認識の下に、素子特性発現上極めて重要である積層界面制御を、高分子材料からなる素子でどの様に達成するかについて鋭意検討をすすめ、有機EL素子の発光層および電荷注入層を高分子体化することによって素子の耐久性を高めると共に、種々の劣化要因あるいは特性発現の規制因子となり易い異種材料からなるヘテロ接合界面をなくし、複数の発光層を同じ高分子材料で構成した一体化ホモ接合多層構造とし、高分子発光層の一部に高分子ドーパントをドーピング処理して電荷注入層とすることにより、安定した高い素子特性と十分な耐久性を兼備した有機EL素子が実現することを確認し、本発明に到達したものである。

【0011】すなわち、本発明は、少なくとも一方が透明である一対の電極間に、有機薄膜発光層を挟持してなる有機薄膜型エレクトロルミネッセント素子において、前記発光層が同一の高分子発光体を少なくとも2層積層したものであって、前記発光体層の少なくとも一つは高分子ドーパントがドーブされた電荷注入層であることを特徴とする有機薄膜エレクトロルミネッセント素子を提供したものである。以下、本発明をより詳細に説明する。

【0012】図1は、本発明の有機薄膜エレクトロルミネッセント素子の1例の概略構成を示す断面図であり、支持基板1上に、透明電極（陽極）2、電荷（正孔）注入層を兼ねた発光層3、発光層4および電極（陰極）5が積層された構造からなっている。

【0013】有機薄膜エレクトロルミネッセント素子の構成としては、上記の他に支持基板上に、透明電極（陽極）、第1の電荷（正孔）注入層、発光層、第2の電荷（電子）注入層および電極（陰極）を積層してなるもの、および同じく支持基板上に、透明電極（陽極）、発光層、電荷（電子）注入層を兼ねた発光層および電極（陰極）を積層してなるものなどがある。

【0014】支持基板1としては透明性を有するものが好ましく、一般にガラス、石英、ポリエチレンテレフタ \*



【0022】（式中、R¹は低級アルキル基、対イオンXはハロゲンイオンを表わす。）で示される水溶性のポリパラキシレンモノスルホニウム塩あるいは有機溶媒可溶性のポリ-α-モノアルコキシジメチレンフェニレンの熱分解により得られ、また構造式[2]のポリナフト

(3)

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\*レートなどの透明樹脂材料が用いられる。また、電極（陽極2および陰極3）としては、金、アルミニウム、インジウムなどの金属、合金、それらの混合物あるいはインジウムチンオキシド（ITO）、SnO<sub>2</sub>、ZnOなどの材料を用いることが好ましい。これらの電極は発光の透過率を高めるため少なくとも一方を透明材料とする。

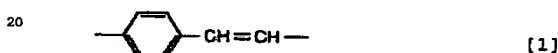
【0015】発光層としては同一の高分子発光体の複数の層を積層したものが用いられる。積層体の1つは高分子発光体のみからなる発光層であり、他の層は高分子ドーパントがドーブされた発光層である。

【0016】本発明で用いられる発光体は高分子発光体であれば特に制限はないが、変調ドーブ構造を実現する上からは、高分子発光体それ自体ないしその前駆体が、水溶性あるいは有機溶媒可溶性であることが望ましい。このような高分子発光体の具体例としては、特に構造式

[1]

【0017】

【化3】

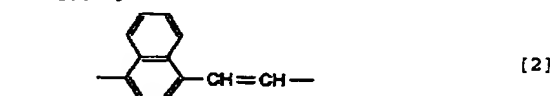


【0018】で示されるポリパラフェニレンビニレン（PPV）骨格を有する高分子化合物および構造式

[2]

【0019】

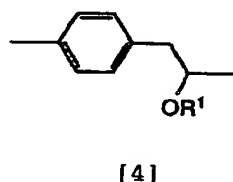
【化4】



【0020】で示されるポリナフトビニレン骨格を有する高分子化合物が好ましい。前記構造式[1]および[2]の高分子発光体はポリアリーレンジメチレンモノスルホニウム塩あるいはポリ-α-モノアルコキシジメチレンアリレンのような前駆体を経由して合成される。すなわち、前記構造式[1]の高分子発光体は下記構造式[3]あるいは[4]

【0021】

【化5】

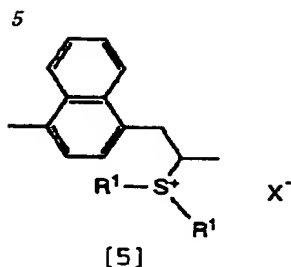


ビニレン骨格を有する高分子化合物は下記構造式[5]あるいは[6]

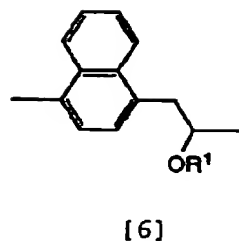
【0023】

【化6】

(4)



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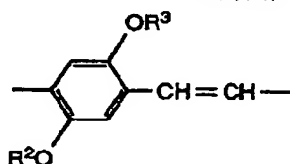


【0024】(式中の記号は前記と同じ意味を表わす。)で示される水溶性のポリナフタレンジメチレンモノスルホニウム塩あるいは有機溶媒可溶性のポリ-1,3-ナフテニル-1'-アルコキシエチニレンの熱分解\*

\*により得られる。さらに、構造式 [7]

【0025】

【化7】

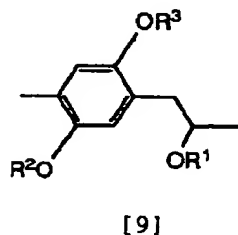
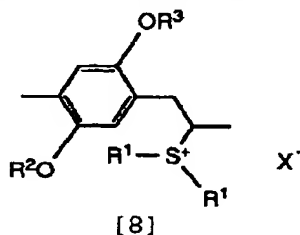


【0026】(式中、R<sup>2</sup> および R<sup>3</sup> はアルキル基を表わす。)で示される構造の高分子化合物も好ましい高分子発光体である。この化合物も前記と同様に構造式

※ [8] あるいは [9]

【0027】

※ 【化8】



【0028】(式中の記号は前記と同じ意味を表わす。)で示される水溶性のポリジアルコキシキシレンモノスルホニウム塩あるいは有機溶媒可溶性のポリ-α-モノアルコキシジメチレンジアルコキシフェニレンの熱分解により得られる。

【0029】また、電荷注入系を形成する為の高分子ドーパントは前記発光層の高分子化合物と同様に水溶性または有機溶媒可溶性のものから選択する。高分子発光体がポリアリーレンビニレンの様な前駆体を経由して合成される導電性高分子の場合には、前駆体溶液に高分子ドーパントを添加した後構造転換処理を行なうことになり、処理条件下でのドーピング状態の安定性もまた必要となる。高分子ドーパントは、ドーピング効果を発現することはもとより、素子駆動中の発熱あるいは前駆体処理過程での加熱に耐える耐熱性を有すること、素子駆動時の印加電場勾配や熱運動によって系中を移動することのない安定性を有することが要件である。この要件を満たす高分子ドーパントの例としては、p型ドーピング用には、ポリスチレンスルホン酸、ポリナフチルスルホン酸等、スルホン酸基を保持する高分子カチオン、またn型ドーピング用にはアンモニウム基を保持する高分子アニ

オンが好適である。

【0030】高分子ドーパントはp型およびn型何れも分子量5万以下のものが好ましい。更に好ましいのは、モノマーとして前駆体溶液中に混合し、熱処理時に同時に熱重合して高分子ドーパントとして機能する系である。その様なものとして、パラスチレンスルホン酸、ビニルスルホン酸などがある。

【0031】素子の構築に当たっては、前記高分子発光層及び電荷注入層を塗布法によって成膜する。この場合、塗布の手法としてはスピナー塗布、ロール塗布、スプレー塗布、浸漬塗布、グラビア塗布等の公知の方法の他、キャストリング法も用いることが出来る。

【0032】変調ドーピング構造の実現のためには、素子構造に応じてドーピング層、非ドーピング層を逐次成膜すればよい。例えば、素子の発光層を正孔注入層、発光層、電子注入層の3層構造とする場合には、先ず、陽極の透明電極(I.T.O等)基板上に高分子アニオンを含有する発光体高分子溶液を塗布成膜して正孔注入層を形成し、次いでドーパント(高分子イオン)を含まない発光層、高分子カチオンを含有する電子注入層を逐次形成して、目的とするホモ多層構造を得る。

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【0033】積層塗布に際しては、発光体高分子の種類、溶媒の種類により一概に決められないが、基本的には半乾燥状態で引続き次の塗布工程に移行することが好ましい。各層の厚みも、発光材料、ドーパント種、溶媒の種類等により、各々のケースによって最適値が定められるが、素子特性発現上、500～3000オングストロームが好適な範囲である。

【0034】

【実施例】以下、実施例を挙げて本発明を説明するが、本発明は以下の例のみに限定されるものではない。

【0035】実施例1

1.5 重量% P P V 前駆体（前記構造式〔3〕においてR1がCH<sub>3</sub>、XがC1の高分子化合物）水溶液にポリスチレンスルホン酸（分子量～8000）を1.5 重量%溶解せしめ、これを電荷（正孔）注入層用 P P V 前駆体溶液とする。この溶液を I T O ガラス基板上に回転塗布法によって塗布し、約1000オングストロームの厚さに成膜し、風乾させた。次に、その上に3重量% P P V 前駆体水溶液を同様に回転塗布によって成膜し、約8000オングストロームの厚みの発光層を形成した。この間作業はクリーンブース内で行ない、界面の汚染を極力防いだ。発光層の風乾の後、アルゴン雰囲気中で2時間、200℃の加熱処理を施し、P P V 前駆体を P P V 構造に転換せしめた。徐冷の後真空蒸着によりアルミニウム電極（陰極）を3000オングストロームの厚みで形成した。銀ペストを用いてリード線を取り付け、素子を完成した。

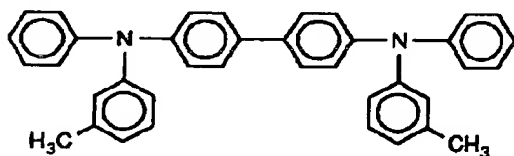
【0036】上記の様に作成した図1に示す E L 素子について、I T O 電極側に正、アルミニウム電極側に負の直流電圧を印加したときの電圧と発光輝度との関係を図2、電流密度と発光輝度との関係を図3、発光輝度の経時変化を図4に示す。

【0037】比較例1

I T O 電極上に P P V 発光層（約8000オングストローム）とアルミニウム電極（陰極）を3000オングストロームを設けた単層構造の E L 素子について実施例1と同様にして直流電圧を印加したときの電圧と発光輝度との関係を図2、電流密度と発光輝度との関係を図3、発光輝度の経時変化を図4に示す。

【0038】比較例2

I T O 電極上に代表的な正孔輸送系である下記構造式〔化9〕



【0039】で示される芳香族ジアミン（TAD）を電

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荷注入層（約1000オングストローム）を真空蒸着法によって設け、その上に有機溶媒可溶性前駆体の塗布および加熱処理によって P P V 発光層（約8000オングストローム）を設け、その後真空蒸着によりアルミニウム電極を3000オングストロームの厚みで形成し、E L 素子を作成した。この E L 素子について実施例1と同様にして直流電圧を印加したときの電圧と発光輝度との関係を図2、電流密度と発光輝度との関係を図3、発光輝度の経時変化を図4に示す。実施例および比較例の発光の挙動から本発明による有機薄膜エレクトロルミネッセント素子での輝度の向上と発光寿命の大幅な延伸が明らかである。

【0040】実施例2

1.5 重量% P P V 前駆体（実施例1に同じもの）水溶液にポリスチレンスルホン酸を1.5 重量%溶解せしめ、これを電荷注入層用 P P V 前駆体水溶液としたこと以外は実施例1と全く同様にして E L 素子を作製した。この例では、ポリスチレンスルホン酸は200℃加熱処理時に熱重合して高分子ドーパントとなる。この素子の発光挙動を測定したところ、実施例1と同様、顕著な輝度の向上と発光寿命の延伸が実現された。

【0041】

【発明の効果】少なくとも一方が透明である一対の電極間に、有機薄膜発光層を挟持してなる有機薄膜型エレクトロルミネッセント素子において、前記発光層が同一の高分子発光体を少なくとも2層積層したものであって、前記発光体層の少なくとも一つを高分子ドーパントがドーパされた電荷注入層とした本発明の有機薄膜エレクトロルミネッセント素子は、塗布成膜法を利用して、きわめて簡便な手法で構築でき、従来の有機 E L 素子の抱える短寿命の問題が解決された長寿命、高効率、耐久性に優れた素子である。

【図面の簡単な説明】

【図1】本発明の有機薄膜エレクトロルミネッセント素子の1例の概略の構成を示す断面図である。

【図2】実施例1の E L 素子および比較例の2種類の E L 素子の電圧と発光輝度の関係を示すグラフである。

【図3】実施例1の E L 素子および比較例の2種類の E L 素子の電流密度と発光輝度の関係を示すグラフである。

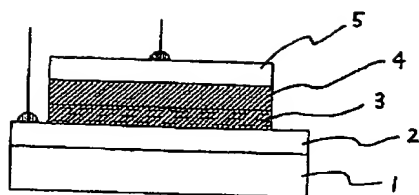
【図4】実施例1の E L 素子および比較例の2種類の E L 素子の発光輝度の経時変化を示すグラフである。

【符号の説明】

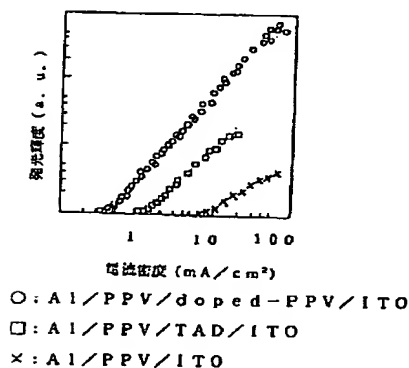
- 1 支持基板
- 2 透明電極（陽極）
- 3 電荷注入層
- 4 発光層
- 5 電極（陰極）

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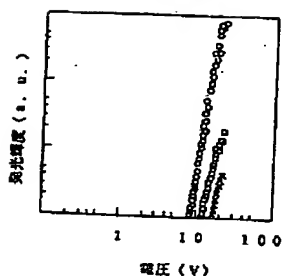
【図1】



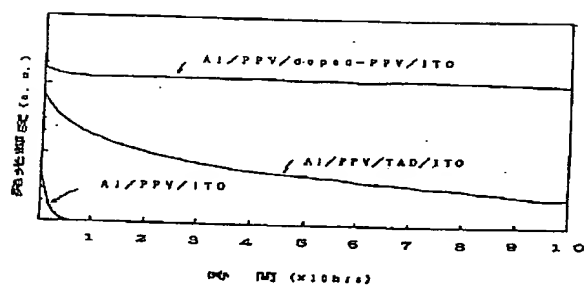
【図3】



【図2】



【図4】



## 【手続補正書】

【提出日】平成5年7月23日

## 【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】請求項1

【補正方法】変更

## 【補正内容】

【請求項1】 少なくとも一方が透明である一対の電極間に、有機薄膜発光層を挟持してなる有機薄膜型エレクトロルミネッセント素子において、前記発光層が同一の高分子発光体を少なくとも2層積層したものであって、前記発光体層の少なくとも一つは高分子ドーパントがドーパされた電荷注入層であることを特徴とする有機薄膜エレクトロルミネッセント素子。

## 【手続補正2】

【補正対象書類名】明細書

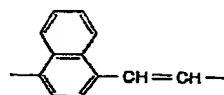
【補正対象項目名】請求項3

【補正方法】変更

## 【補正内容】

【請求項3】 発光体が構造式〔2〕

【化2】



〔2〕

で表されるポリ-1,4-ナフテニレンビニレン骨格を有する高分子化合物である請求項第1項に記載の有機エレクトロルミネッセント素子。

## 【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】請求項4

【補正方法】変更

## 【補正内容】

【請求項4】 発光層が塗布法により形成されてなる層である請求項第1項乃至第3項のいずれかの項に記載の有機エレクトロルミネッセント素子。

## 【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0013

【補正方法】変更

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## 【補正内容】

【0013】 本発明による有機薄膜エレクトロルミネッセント素子の構成としては、上記の他に支持基板上に、透明電極（陽極）、第1の電荷（正孔）注入層、発光層、第2の電荷（電子）注入層および電極（陰極）を積層してなるもの、および同じく支持基板上に、透明電極（陽極）、発光層、電荷（電子）注入層を兼ねた発光層および電極（陰極）を積層してなるものなどがある。

## 【手続補正5】

【補正対象書類名】明細書

【補正対象項目名】0014

【補正方法】変更

## 【補正内容】

【0014】 支持基板1としては透明性を有するものが好ましく、一般にガラス、石英、ポリエチレンテレフタレートなどの透明樹脂材料が用いられる。また、電極（陽極2および陰極5）としては、金、アルミニウム、インジウムなどの金属、合金、それらの混合物あるいはインジウムチンオキサイド（ITO）、 $\text{SnO}_2$ 、 $\text{ZnO}$ などの材料を用いることが好ましい。これらの電極は発光の透過率を高めるため少なくとも一方を透明材料とする。

## 【手続補正6】

【補正対象書類名】明細書

【補正対象項目名】0015

【補正方法】変更

## 【補正内容】

【0015】 本発明において前記発光層としては同一の高分子発光体の複数の層を積層したものが用いられる。積層体の1つは高分子発光体のみからなる発光層であり、他の層は高分子ドーパントがドーパされた発光層である。

## 【手続補正7】

【補正対象書類名】明細書

【補正対象項目名】0020

【補正方法】変更

## 【補正内容】

【0020】 で示されるポリ-1,4-ナフテニレンビニレン骨格を有する高分子化合物が好ましい。前記構造式[1]および[2]の高分子発光体はポリアリーレン-1',2'-エチレン-1'-スルホニウム塩あるいはポリアリーレン-1'-アルコキシ-1',2'-エチレンのような前駆体を経由して合成される。すなわち、前記構造式[1]の高分子発光体は下記構造式[3]あるいは[4]

## 【手続補正8】

【補正対象書類名】明細書

【補正対象項目名】0022

【補正方法】変更

## 【補正内容】

【0022】 （式中、 $R^1$ は低級アルキル基、対イオン $X^-$ はハロゲンイオンを表わす。）で示される水溶性のポリ-1,4-フェニレン-1',2'-エチレン-1'-スルホニウム塩あるいは有機溶媒可溶性のポリ-1,4-フェニレン-1'-アルコキシ-1',2'-エチレンの熱分解により得られ、また構造式[2]のポリ-1,4-ナフテニレンビニレン骨格を有する高分子化合物は下記構造式[5]あるいは[6]

## 【手続補正9】

【補正対象書類名】明細書

【補正対象項目名】0024

【補正方法】変更

## 【補正内容】

【0024】 （式中の記号は前記と同じ意味を表わす。）で示される水溶性のポリ-1,4-ナフテニレン-1',2'-エチレン-1'-スルホニウム塩あるいは有機溶媒可溶性のポリ-1,4-ナフテニレン-1'-アルコキシ-1',2'-エチレンの熱分解により得られる。さらに、構造式[7]

## 【手続補正10】

【補正対象書類名】明細書

【補正対象項目名】0028

【補正方法】変更

## 【補正内容】

【0028】 （式中の記号は前記と同じ意味を表わす。）で示される水溶性のポリ-2,5-ジアルコキシ-1,4-フェニレン-1',2'-エチレン-1'-スルホニウム塩あるいは有機溶媒可溶性のポリ-2,5-ジアルコキシ-1,4-フェニレン-1'-アルコキシ-1',2'-エチレンとの熱分解により得られる。

## 【手続補正11】

【補正対象書類名】明細書

【補正対象項目名】0029

【補正方法】変更

## 【補正内容】

【0029】 また、電荷注入系を形成する為の高分子ドーパントは前記発光層の高分子化合物と同様に水溶性または有機溶媒可溶性のものから選択する。高分子発光体がポリアリーレンビニレンの様な前駆体を経由して合成される導電性高分子の場合には、前駆体溶液に高分子ドーパントを添加した後構造転換処理を行なうことになり、高分子ドーパントとしては、処理条件下でのドーパ状態の安定性もまた必要となる。それゆえ高分子ドーパントは、ドーピング効果を発現することはもとより、素子駆動中の発熱あるいは前駆体処理過程での加熱に耐える耐熱性を有すること、素子駆動時の印加電場勾配や熱運動によって系中を移動することのない安定性を有することが要件である。この要件を満たす高分子ドーパントの例としては、p型ドーピング用には、ポリスチレンスルホン酸、ポリナフチルスルホン酸等、スルホン酸基を



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保持する高分子カチオン、また n 型ドーピング用にはアンモニウム基を保持する高分子アニオンが好適である。

【手続補正 1 2】

【補正対象書類名】明細書

【補正対象項目名】図 2

【補正方法】変更

【補正内容】

【図 2】 実施例 1 の E L 素子および 2 種類の比較例 の E L 素子の電圧と発光輝度の関係を示すグラフである。

【手続補正 1 3】

【補正対象書類名】明細書

【補正対象項目名】図 3

【補正方法】変更

【補正内容】

【図 3】 実施例 1 の E L 素子および 2 種類の比較例 の E L 素子の電流密度と発光輝度の関係を示すグラフである。

【手続補正 1 4】

【補正対象書類名】明細書

【補正対象項目名】図 4

【補正方法】変更

【補正内容】

【図 4】 実施例 1 の E L 素子および 2 種類の比較例 の E L 素子の発光輝度の経時変化を示すグラフである。

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3. In the drawings, any words are not translated.

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CLAIMS

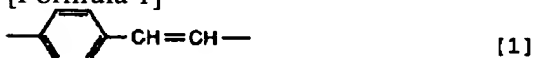
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[Claim(s)]

[Claim 1] It is the organic thin film electroluminescent element which at least one side carries out the two-layer laminating of the macromolecule emitter with said same luminous layer to inter-electrode [ of a transparent couple ] at least in the organic thin film mold electroluminescent element which comes to pinch an organic thin film luminous layer, and is characterized by at least one of said the emitter layers being the charge impregnation layer by which macromolecule DOPANNT0 was doped.

[Claim 2] An emitter is a structure expression [1].

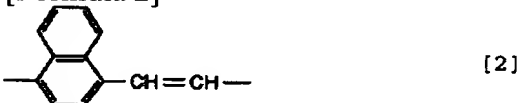
[Formula 1]



An organic electroluminescent element given in the 1st term of a claim which is the high molecular compound which comes out and has the poly para-phenylene vinylene frame expressed.

[Claim 3] An emitter is a structure expression [2].

[Formula 2]



An organic electroluminescent element given in the 2nd term of a claim which is the high molecular compound which comes out and has the poly naphth vinylene frame expressed.

[Claim 4] An organic electroluminescent element given in the 3rd term of a claim or the 4th term whose luminous layer is a layer which it comes to form by the applying method.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to an organic thin film electroluminescent (it omits Following EL.) component. Furthermore, if it says in detail, it has high brightness and an efficient luminescence property, and is related with an organic thin film EL element available as field-like the light source and a display device.

[0002]

[Description of the Prior Art] An EL element is also called electroluminescence devices and the application study as a field-like emitter is performed extensively. This EL element is divided roughly into two by the difference in a luminescence excitation device. One is an intrinsic (proper) EL element based on the so-called DESUTORIO (Destriau) effectiveness which emits light only by impression of strong electric field, and other one is charge injection EL based on the so-called ROZEFU (Lossev) effectiveness which emits light by passing the forward current to point contact diode or pn junction.

[0003] The system of the former which carried out addition distribution of the element used as the emission center (active ingredient) of Mn, Cu, rare earth elements, etc. is common to II-VI group compound semiconductors, such as ZnS and CdS, and the active ingredient excitation by the hot electron is considered to be fundamental luminescent mechanism. The research on this kind of EL element has long history and a real product, the distributed component is already put in practical use, and research of a thin film mold component has also been briskly done after the 1970s.

[0004] However, the EL element which consists of the above-mentioned inorganic material has the high manufacturing cost of that high electric-field impression of 200V is the need, and a circumference actuation circuit to actuation, and many troubles -- that endurance and brightness are imperfection and multiple-colorizing is difficult -- are held.

[0005] On the other hand, about the charge impregnation mold EL element, although research is done for the organic compound centering on condensed multi-ring aromatic hydrocarbon for many years, it became in the end of the 1970s and the measure from a practical standpoint has been made. The greatest description of a charge impregnation mold EL element is in the point in which actuation on a low electrical potential difference is possible compared with said intrinsic EL component.

[0006] Very much at the second half of the 1980s by the formation of a homogeneity thin film of the ingredient by vacuum deposition membrane formation, and laminating multilayering of a charge impregnation layer and a luminous layer It was proved that the charge impregnation mold EL element which uses an organic thin film as an emitter could turn into high brightness and an efficient outstanding field-like light emitting device. C.W.Tang et al., Appl.Phys.Lett., 51, and 913 (1987) -- [ for example, ] C.Adachi et al., Jpn.J.Appl.Phys., 27, L269 (1988), and JP,59-194393,A U.S. Pat. No. 4,720,432 etc. . moreover, variegated color tone control according to substituent installation taking advantage of the versatility of a molecular design peculiar to an organic material -- possible -- the intrinsic EL component of an inorganic material -- it should also wish -- it is also shown that \*\*\*\*\* of EL coloring which is not is made (C.Adachi et al., Appl.Phys.Lett., 56, and 799 (1990)).

[0007] Although the engine performance of the like which, as for a part of these organic thin film mold EL element, exceeds practical use level in a component property which should be \*\* carried out is obtained, a life is short and has the big fault that endurance is scarce. By the vacuum deposition film, this has a main cause in condensation of a molecule taking place and ununiformity-izing by energization, with time, and is carrying out the failure to utilization to the demand of homogeneity vacuum evaporatio no membrane formation ability adding a severe limit to ingredient selection conjointly at the serious thing.

[0008] As a leading means for attaining the reinforcement, it is possible to form an ingredient into a macromolecule object, harnessing the features of an organic EL device. Recently, the attempt which EL luminescence by poly para-phenylene vinylene (PPV) is checked (J.H.Brurroughes et al, Nature, 347,539 (1990), WO-9013148, etc.), and applies an electric conduction macromolecule to a charge impregnation layer is also performed (S.Adachi et al., Jpn.J.Appl., Phys., 25, and L773 (1986)). On the other hand, means, such as using the mixed thin film which unified the luminous layer and the charge impregnation layer, are also provided (please join, if there is reference.). However, neither comes to acquire a sufficient component property and a sufficient life, and the actual condition is far from a practical use region.

[0009]

[Problem(s) to be Solved by the Invention] Therefore, this invention solves the above-mentioned trouble and it aims at offering the organic thin film mold EL element which combines high brightness, an efficient property, and sufficient endurance.

[0010]

[Means for Solving the Problem] this invention persons set to an organic thin film mold electroluminescent element. Under recognition that macromolecule object-ization of a component component is indispensable requirements in order to realize necessary endurance Examination is wholeheartedly recommended about how very important laminating interface control is attained on a component property manifestation with the component which consists of polymeric materials. While raising the endurance of a component by forming the luminous layer and charge impregnation layer of an organic EL device into a macromolecule object The heterojunction interface which consists of a dissimilar material which is easy to serve as various degradation factors or a regulation factor of a property manifestation is abolished. By considering as the unification gay junction multilayer structure which constituted two or more luminous layers from same polymeric materials, carrying out doping processing of the macromolecule dopant, and considering as a charge impregnation layer at a part of macromolecule luminous layer It checks that the organic EL device which combined the stable high component property and sufficient endurance is realized, and this invention is reached.

[0011] That is, this invention carries out the two-layer laminating of the macromolecule emitter with said same luminous layer to inter-electrode [ of a couple at least with transparent one side ] at least in the organic thin film mold electroluminescent element which comes to pinch an organic thin film luminous layer, and at least one of said the emitter layers offers the organic thin film electroluminescent element characterized by being the charge impregnation layer by which the macromolecule dopant was doped. Hereafter, this invention is explained more to a detail.

[0012] Drawing 1 is the sectional view showing the outline configuration of one example of the organic thin film electroluminescent element of this invention, and consists of structure where the laminating of the luminous layer 3, the luminous layer 4, and electrode (cathode) 5 which served both as the transparent electrode (anode plate) 2 and the charge (electron hole) impregnation layer on the support substrate 1 was carried out.

[0013] Similarly as a configuration of an organic thin film electroluminescent element, there is a thing which comes to carry out the laminating of the thing which comes to carry out the laminating of a transparent electrode (anode plate), the 1st charge (electron hole) impregnation layer, a luminous layer, the 2nd charge (electron) impregnation layer, and the electrode (cathode), the luminous layer which served both as the transparent electrode (anode plate), the luminous layer, and the charge (electron) impregnation layer on the support substrate, and the electrode (cathode) on [ other than the above ] a support substrate.

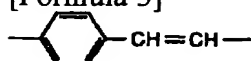
[0014] What has transparency as a support substrate 1 is desirable, and, generally transparenance resin ingredients, such as glass, a quartz, and polyethylene terephthalate, are used. Moreover, as an electrode (an anode plate 2 and cathode 3), it is desirable to use ingredients, such as metals, such as gold, aluminum, and an indium, alloys, those mixture or indium tin oxide (ITO), SnO<sub>2</sub>, and ZnO. These electrodes make at least one side a transparent material in order to raise the permeability of luminescence.

[0015] What carried out the laminating of two or more layers of the macromolecule emitter same as a luminous layer is used. One of the layered products is a luminous layer which consists only of a macromolecule emitter, and other layers are luminous layers by which the macromolecule dopant was doped.

[0016] Although there will be especially no limit if the emitter used by this invention is a macromolecule emitter, from from [ when realizing modulation dope structure ], it is desirable for macromolecule emitter itself thru/or its precursor to be water solubility or organic solvent fusibility. Especially as an example of such a macromolecule emitter, it is a structure expression [ 1 ].

[0017]

[Formula 3]

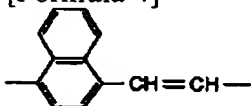


[1]

[0018] The high molecular compound and structure expression [2] which come out and have the poly para-phenylene vinylene (PPV) frame shown

[0019]

[Formula 4]

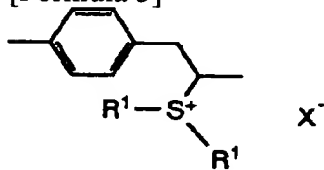


[2]

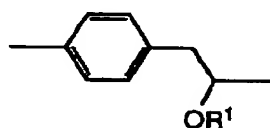
[0020] The high molecular compound which comes out and has the poly naphth vinylene frame shown is desirable. Said structure expression [1] and the giant-molecule illuminant of [2] are compounded via PORIARIREN dimethylene mono-sulfonium salt or a precursor like Polly alpha-mono-alkoxy dimethylene propine. That is, the macromolecule emitter of said structure expression [1] is the following structure expression [3] or [4].

[0021]

[Formula 5]



[3]

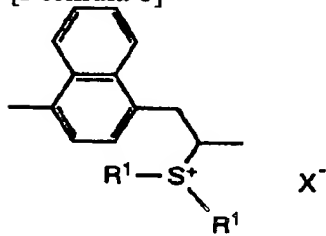


[4]

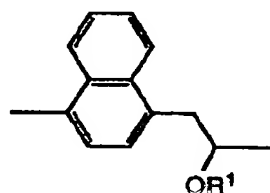
[0022] (-- in R1, low-grade alkyl group and counter ion X expresses halogen ion among a formula.) -- the high molecular compound which is obtained by the pyrolysis of the Polly alpha-mono-alkoxy dimethylene phenylene of the water-soluble poly paraxylene mono-sulfonium salt shown or organic solvent fusibility, and has the poly naphth vinylene frame of a structure expression [2] -- the following structure expression [5] or [6]

[0023]

[Formula 6]



[5]

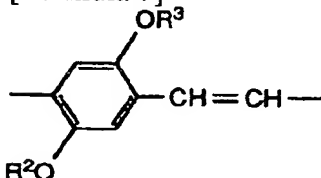


[6]

[0024] (-- the notation in a formula expresses the same semantics as the above.) -- it is obtained by Polly 1 of the water-soluble PORINAFUTAREN dimethylene mono-sulfonium salt shown or organic solvent fusibility, and the pyrolysis of 3-NAFUTENIRU-1'-alkoxy ethynylene. Furthermore, a structure expression [7]

[0025]

[Formula 7]



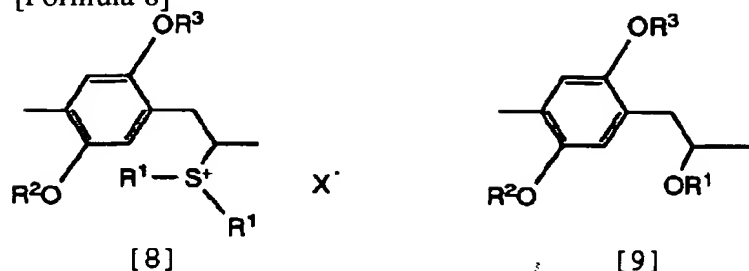
[7]

[0026] (-- R2 and R3 express an alkyl group among a formula.) -- the high molecular compound of the structure shown is also a desirable macromolecule emitter. It is a structure expression [8] or [9] like [ this

compound ] the above.

[0027]

[Formula 8]



[0028] (-- the notation in a formula expresses the same semantics as the above.) -- it is obtained by the pyrolysis of the Polly alpha-MONOARUKOKISHI dimethylene dialkoxy phenylene of the water-soluble poly dialkoxy KISHIREMMONO sulfonium salt shown or organic solvent fusibility.

[0029] Moreover, the macromolecule dopant for forming a charge impregnation system is chosen from the thing of water solubility or organic solvent fusibility like the high molecular compound of said luminous layer. In the case of the conductive polymer by which a giant-molecule illuminant is compounded via a precursor like the poly arylene vinylene, after adding a giant-molecule dopant in a precursor solution, structural transformation processing will be performed, and the stability of the dope condition under processing conditions is also needed for it. It is requirements that that a macromolecule dopant discovers the doping effectiveness has the thermal resistance which is equal to generation of heat under component actuation or heating by the precursor processing process from the first, and to have the stability which does not move in the inside of a system by the impression electric field gradient or thermal motion at the time of component actuation. As an example of the giant-molecule dopant which satisfies this requirement, the giant-molecule anion holding ammonium is suitable for the giant-molecule cation which holds sulfonic groups, such as polystyrene sulfonate and the poly naphthyl sulfonic acid, with p mold doping, and n mold doping.

[0030] a macromolecule dopant -- p mold and n mold -- all have a with a molecular weight of 50,000 or less desirable thing. Furthermore, the system which is mixed in a precursor solution as a monomer, carries out thermal polymerization simultaneously at the time of heat treatment, and functions as a macromolecule dopant is desirable. The Pallas CHIREN sulfonic acid, a vinyl sulfonic acid, etc. are one of such things.

[0031] In construction of a component, said macromolecule luminous layer and a charge impregnation layer are formed by the applying method. In this case, as the technique of spreading, the casting method besides well-known approaches, such as spinner spreading, roll coating, spray spreading, a dip painting cloth, and gravure spreading, can also be used.

[0032] What is necessary is just to form a dope layer and a non-doping layer serially according to component structure for implementation of modulation dope structure. For example, in making the luminous layer of a component into the three-tiered structure of a hole injection layer, a luminous layer, and an electronic injection layer, first, spreading membrane formation of the emitter polymer solution containing a macromolecule anion is carried out, a hole injection layer is formed on the transparent electrode substrates (ITO etc.) of an anode plate, the luminous layer which subsequently does not contain a dopant (macromolecule ion), and the electronic injection layer containing a macromolecule cation are formed serially, and it acquires the gay multilayer structure made into the object.

[0033] Although not generally decided according to the class of emitter macromolecule, and the class of solvent on the occasion of laminating spreading, it is desirable to shift to the following spreading process succeedingly in half-dryness fundamentally. The thickness of each class is also the range where 500-3000Å is suitable on a component property manifestation, although an optimum value is defined by the class of luminescent material, a dopant kind, and solvent etc. in each case.

[0034]

[Example] Although an example is given and this invention is explained hereafter, this invention is not limited only to the following examples.

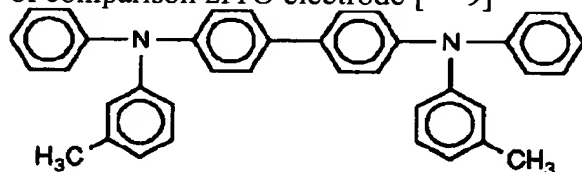
[0035] Example 11.5 It is polystyrene sulfonate (molecular weight -8000) to a weight %PPV precursor (it sets in said structure expression [3], and, for R1, CH3 and X are high molecular compound of Cl) water solution 1.5 Do the weight % dissolution of and let this be a PPV precursor solution for charge (electron hole) impregnation layers. This solution was applied by the revolution applying method on the ITO glass

substrate, and the air dried was formed membranes and carried out to the thickness of about 1000Å. Next, on it, the PPV precursor water solution was similarly formed by revolution spreading 3% of the weight, and the luminous layer with a thickness of about 8000Å was formed. This intercropping business was performed in the clean booth, and prevented contamination of an interface as much as possible. 200-degree C heat-treatment was performed in argon atmosphere after the air dried of a luminous layer for 2 hours, and the PPV precursor was made to convert into PPV structure. The aluminum electrode (cathode) was formed by the thickness of 3000Å with vacuum deposition after annealing. Lead wire was attached using the silver paste and the component was completed.

[0036] Aging of drawing 3 and luminescence brightness is shown [ the relation between the electrical potential difference when impressing negative direct current voltage to an ITO electrode side at a forward and aluminum electrode side about the EL element shown in drawing 1 created as mentioned above, and luminescence brightness ] for the relation between drawing 2 , current density, and luminescence brightness in drawing 4 .

[0037] Aging of drawing 3 and luminescence brightness is shown [ the relation between the electrical potential difference when impressing direct current voltage like an example 1 on an example of comparison 1 ITO electrode about the EL element of monolayer structure which prepared 3000Å for the PPV luminous layer (about 8000Å) and the aluminum electrode (cathode), and luminescence brightness ] for the relation between drawing 2 , current density, and luminescence brightness in drawing 4 .

[0038] The following structure expression which is an electron hole transport system typical on an example of comparison 2 ITO electrode [\*\* 9]



[0039] It came out, the charge impregnation layer (about 1000Å) was prepared for the aromatic series diamine (TAD) shown with the vacuum deposition method, the PPV luminous layer (about 8000Å) was prepared by spreading and heat-treatment of an organic solvent fusibility precursor on it, the aluminum electrode was formed by the thickness of 3000Å with vacuum deposition after that, and the EL element was created. Aging of drawing 3 and luminescence brightness is shown [ the relation between the electrical potential difference when impressing direct current voltage like an example 1 about this EL element, and luminescence brightness ] for the relation between drawing 2 , current density, and luminescence brightness in drawing 4 . The large drawing of improvement in the brightness in the organic thin film electroluminescent element by this invention and a luminescence life is clear from the behavior of luminescence of an example and the example of a comparison.

[0040] Example 21.5 It is the Pallas CHIREN sulfonic acid to a weight %PPV precursor (same thing as example 1) water solution 1.5 The EL element was produced completely like the example 1 except having done the weight % dissolution of and having made this into the PPV precursor water solution for charge impregnation layers. In this example, at the time of 200-degree-C heat-treatment, the thermal polymerization of the Pallas CHIREN sulfonic acid is carried out, and it serves as a macromolecule dopant. When the luminescence behavior of this component was measured, improvement in remarkable brightness and the drawing of a luminescence life were realized like the example 1.

[0041]

[Effect of the Invention] In the organic thin film mold electroluminescent element with which at least one side comes to pinch an organic thin film luminous layer to inter-electrode [ of a transparent couple ] Said luminous layer carries out the two-layer laminating of the same macromolecule emitter at least. The organic thin film electroluminescent element of this invention which used at least one of said the emitter layers as the charge impregnation layer by which the macromolecule dopant was doped It is the component excellent in long lasting [ by which the problem of the short life which can build by very simple technique and the conventional organic EL device holds using the spreading forming-membranes method was solved ], a well head, and endurance.

[Translation done.]

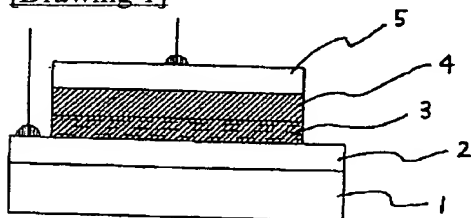
## \* NOTICES \*

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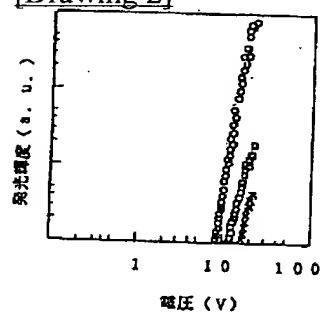
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## DRAWINGS

[Drawing 1]



[Drawing 2]

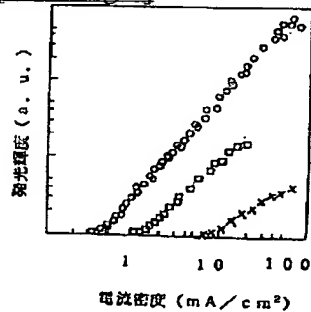


○: Al/PPV/doped-PPV/ITO

□: Al/PPV/TAD/ITO

x: Al/PPV/ITO

[Drawing 3]



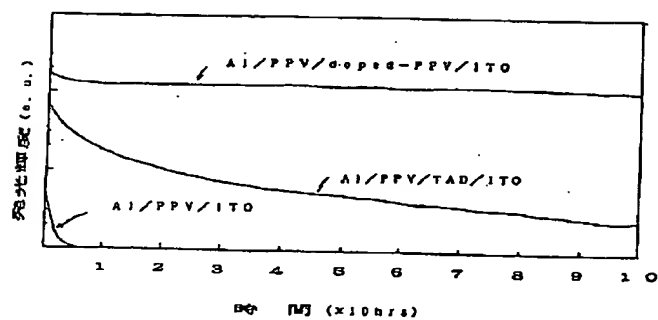
○: Al/PPV/doped-PPV/ITO

□: Al/PPV/TAD/ITO

x: Al/PPV/ITO

[Drawing 4]





[Translation done.]

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## WRITTEN AMENDMENT

----- [procedure amendment]

[Filing Date] July 23, Heisei 5

[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claim 1

[Method of Amendment] Modification

[Proposed Amendment]

[Claim 1] It is the organic thin film electroluminescent element which at least one side carries out the two-layer laminating of the macromolecule emitter with said same luminous layer to inter-electrode [ of a transparent couple ] at least in the organic thin film mold electroluminescent element which comes to pinch an organic thin film luminous layer, and is characterized by at least one of said the emitter layers being the charge impregnation layer by which the macromolecule dopant was doped.

[Procedure amendment 2]

[Document to be Amended] Description

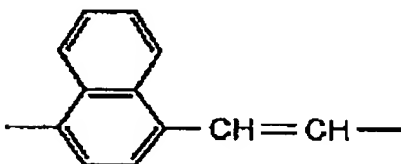
[Item(s) to be Amended] Claim 3

[Method of Amendment] Modification

[Proposed Amendment]

[Claim 3] An emitter is a structure expression [2].

[Formula 2]



[2]

An organic electroluminescent element given in the 1st term of a claim which is the high molecular compound which comes out and has Polly 1 and 4-NAFUTENIREN vinylene frame which are expressed.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] Claim 4

[Method of Amendment] Modification

[Proposed Amendment]

[Claim 4] An organic electroluminescent element given in the term of either the 1st term of a claim whose luminous layer is a layer which it comes to form by the applying method thru/or the 3rd term.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0013

[Method of Amendment] Modification

[Proposed Amendment]

[0013] As a configuration of the organic thin film electroluminescent element by this invention On [ other than the above ] a support substrate, a transparent electrode (anode plate), the 1st charge (electron hole) impregnation layer, Similarly there is a thing which comes to carry out the laminating of the thing which comes to carry out the laminating of a luminous layer, the 2nd charge (electron) impregnation layer, and the

electrode (cathode), the luminous layer which served both as the transparent electrode (anode plate), the luminous layer, and the charge (electron) impregnation layer, and the electrode (cathode) on a support substrate.

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0014

[Method of Amendment] Modification

[Proposed Amendment]

[0014] What has transparency as a support substrate 1 is desirable, and, generally transparency resin ingredients, such as glass, a quartz, and polyethylene terephthalate, are used. Moreover, as an electrode (an anode plate 2 and cathode 5), it is desirable to use ingredients, such as metals, such as gold, aluminum, and an indium, alloys, those mixture or indium tin oxide (ITO), and SnO<sub>2</sub>, ZnO. These electrodes make at least one side a transparent material in order to raise the permeability of luminescence.

[Procedure amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0015

[Method of Amendment] Modification

[Proposed Amendment]

[0015] What carried out the laminating of two or more layers of the macromolecule emitter same as said luminous layer in this invention is used. One of the layered products is a luminous layer which consists only of a macromolecule emitter, and other layers are luminous layers by which the macromolecule dopant was doped.

[Procedure amendment 7]

[Document to be Amended] Description

[Item(s) to be Amended] 0020

[Method of Amendment] Modification

[Proposed Amendment]

[0020] It comes out and Polly 1 shown and the high molecular compound which has 4-NAFUTENIREN vinylene frame are desirable. Said structure expression [1] and the giant-molecule illuminant of [2] are the poly arylene. - It is 1' and 2'-ethylene-1'-sulfonium salt or poly arylene-1'-alkoxy. - It is compounded via a precursor like 1' and 2'-ethylene. That is, the macromolecule emitter of said structure expression [1] is the following structure expression [3] or [4].

[Procedure amendment 8]

[Document to be Amended] Description

[Item(s) to be Amended] 0022

[Method of Amendment] Modification

[Proposed Amendment]

[0022] the inside of a formula, and R1 -- a low-grade alkyl group -- counter ion X- expresses halogen ion. Water-soluble Polly 1 shown, 4-phenylene - Polly 1 of 1' and 2'-ethylene-1'-sulfonium salt or organic solvent fusibility, 4-phenylene-1'-alkoxy - It is obtained by the pyrolysis of 1' and 2'-ethylene. Moreover, the high molecular compound which has Polly 1 of a structure expression [2] and 4-NAFUTENIREN vinylene frame is the following structure expression [5] or [6].

[Procedure amendment 9]

[Document to be Amended] Description

[Item(s) to be Amended] 0024

[Method of Amendment] Modification

[Proposed Amendment]

[0024] (-- the notation in a formula expresses the same semantics as the above.) -- it is obtained by the pyrolysis of Polly [ of water-soluble Polly / who is shown / 1, 4-NAFUTENIREN-1', and 2'-ethylene-1'-sulfonium salt or organic solvent fusibility ] 1, and 4-NAFUTENIREN-1'-alkoxy-1', and 2'-ethylene. Furthermore, a structure expression [7]

[Procedure amendment 10]

[Document to be Amended] Description

[Item(s) to be Amended] 0028

[Method of Amendment] Modification

[Proposed Amendment]

[0028] (-- the notation in a formula expresses the same semantics as the above.) -- water-soluble Polly 2 shown and 5-dialkoxy -- it is obtained by the pyrolysis with Polly [ of -1, 4-phenylene-1', and 2'-ethylene-1'-sulfonium salt or organic solvent fusibility ] 2, 5-dialkoxy-1, and 4-phenylene-1'-alkoxy-1', and 2'-ethylene.

[Procedure amendment 11]

[Document to be Amended] Description

[Item(s) to be Amended] 0029

[Method of Amendment] Modification

[Proposed Amendment]

[0029] Moreover, the macromolecule dopant for forming a charge impregnation system is chosen from the thing of water solubility or organic solvent fusibility like the high molecular compound of said luminous layer. In the case of the conductive polymer by which a giant-molecule illuminant is compounded via a precursor like the poly arylene vinylene, after adding a giant-molecule dopant in a precursor solution, structural transformation processing will be performed, and as a giant-molecule dopant, the stability of the dope condition under processing conditions is also needed for it. So, it is requirements that that a macromolecule dopant discovers the doping effectiveness has the thermal resistance which is equal to generation of heat under component actuation or heating by the precursor processing process from the first, and to have the stability which does not move in the inside of a system by the impression electric field gradient or thermal motion at the time of component actuation. As an example of the giant-molecule dopant which satisfies this requirement, the giant-molecule anion holding ammonium is suitable for the giant-molecule cation which holds sulfonic groups, such as polystyrene sulfonate and the poly naphthyl sulfonic acid, with p mold doping, and n mold doping.

[Procedure amendment 12]

[Document to be Amended] Description

[Item(s) to be Amended] drawing 2

[Method of Amendment] Modification

[Proposed Amendment]

[Drawing 2] It is the graph which shows the electrical potential difference of the EL element of an example 1, and the EL element of two kinds of examples of a comparison, and the relation of luminescence brightness.

[Procedure amendment 13]

[Document to be Amended] Description

[Item(s) to be Amended] drawing 3

[Method of Amendment] Modification

[Proposed Amendment]

[Drawing 3] It is the graph which shows the relation between the current density of the EL element of an example 1, and the EL element of two kinds of examples of a comparison, and luminescence brightness.

[Procedure amendment 14]

[Document to be Amended] Description

[Item(s) to be Amended] drawing 4

[Method of Amendment] Modification

[Proposed Amendment]

[Drawing 4] It is the graph which shows aging of the luminescence brightness of the EL element of an example 1, and the EL element of two kinds of examples of a comparison.

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[Translation done.]

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## CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law

[Category partition] The 3rd partition of the 3rd category

[Publication date] February 6, Heisei 13 (2001. 2.6)

[Publication No.] JP,6-33048,A

[Date of Publication] February 8, Heisei 6 (1994. 2.8)

[Annual volume number] Open patent official report 6-331

[Application number] Japanese Patent Application No. 4-210902

[The 7th edition of International Patent Classification]

C09K 11/06

H05B 33/14

[FI]

C09K 11/06 Z

H05B 33/14

[Procedure amendment]

[Filing Date] July 9, Heisei 11 (1999. 7.9)

[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claim

[Method of Amendment] Modification

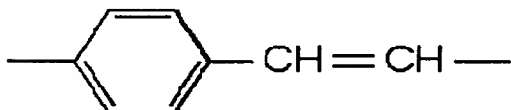
[Proposed Amendment]

[Claim(s)]

[Claim 1] It is the organic thin film electroluminescent element which at least one side carries out the two-layer laminating of the macromolecule emitter with said same luminous layer to inter-electrode [ of a transparent couple ] at least in the organic thin film mold electroluminescent element which comes to pinch an organic thin film luminous layer, and is characterized by at least one of said the emitter layers being the charge impregnation layer by which the macromolecule dopant was doped.

[Claim 2] An emitter is a structure expression [1].

[Formula 1]

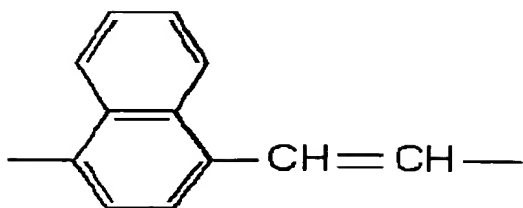


[ 1 ]

An organic electroluminescent element given in the 1st term of a claim which is the high molecular compound which comes out and has the poly para-phenylene vinylene frame expressed.

[Claim 3] An emitter is a structure expression [2].

[Formula 2]



[ 2 ]

An organic electroluminescent element given in the 1st term of a claim which is the high molecular compound which comes out and has Poly 1 and 4-NAFUTENIREN vinylene frame which are expressed.

[Claim 4] An organic electroluminescent element given in the term of either the 1st term of a claim whose luminous layer is a layer which it comes to form by the applying method thru/or the 3rd term.

[Claim 5] In the manufacture approach of an organic thin film mold electroluminescent element that at least one side comes to pinch an organic thin film luminous layer to inter-electrode [ of a transparent couple ] Said luminous layer carries out the two-layer laminating of the same macromolecule emitter at least. The manufacture approach of the organic thin film mold electroluminescent element characterized by including the process to which at least one of said the emitter layers applies the solution with which the macromolecule dopant was added by the water solution or the organic solution of said emitter thru/or its precursor.

[Claim 6] The precursor of an illuminant is Pori Ali-Wren. - 1' and 2'-ethylene-1'-sulfonium salt or Pori Ali-Wren-1'-alkoxy - The manufacture approach of an organic thin film mold electroluminescent element given in the 5th term of a claim which is 1' and 2'-ethylene.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0008

[Method of Amendment] Modification

[Proposed Amendment]

[0008] As a leading means for attaining the reinforcement, it is possible to form an ingredient into a macromolecule object, harnessing the features of an organic EL device. Recently, the attempt which EL luminescence by poly para-phenylene vinylene (PPV) is checked (J.H.Brurroughes et al, Nature, 347,539 (1990), WO-9013148, etc.), and applies an electric conduction macromolecule to a charge impregnation layer is also performed (S.Adachi et al., Jpn.J.Appl., Phys., 25, and L773 (1986)). On the other hand, means, such as using the mixed thin film which unified the luminous layer and the charge impregnation layer, are also provided. However, neither comes to acquire a sufficient component property and a sufficient life, and the actual condition is far from a practical use region.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0037

[Method of Amendment] Modification

[Proposed Amendment]

[0037] The example 1 of a comparison

Aging of drawing 3 and luminescence brightness is shown [ the relation between the electrical potential difference when impressing direct current voltage like an example 1 on an ITO electrode about the EL element of monolayer structure which prepared the PPV luminous layer (about 8000A) and the aluminum electrode (cathode and 3000A), and luminescence brightness ] for the relation between drawing 2, current density, and luminescence brightness in drawing 4.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0039

[Method of Amendment] Modification

[Proposed Amendment]

[0039] It came out, the charge impregnation layer (about 1000A) of aromatic series diamine (TAD) shown was prepared with the vacuum deposition method, the PPV luminous layer (about 8000A) was prepared by spreading and heat-treatment of an organic solvent fusibility precursor on it, the aluminum electrode was formed by the thickness of 3000A with vacuum deposition after that, and the EL element was created.

Aging of drawing 3 and luminescence brightness is shown [ the relation between the electrical potential difference when impressing direct current voltage like an example 1 about this EL element, and

luminescence brightness ] for the relation between drawing 2, current density, and luminescence brightness in drawing 4. The large drawing of improvement in the brightness in the organic thin film electroluminescent element by this invention and a luminescence life is clear from the behavior of luminescence of an example and the example of a comparison.

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[Translation done.]

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